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A failing of coupled-states calculations for inelastic and pressure-broadening cross sections: Calculations on CO 2 –Ar

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A failing of coupled-states calculations for inelastic and pressure-broadening cross sections: Calculations on CO₂-Ar

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Fully quantal benchmark calculations of pressure-broadening cross sections for infrared and Raman lines of CO₂ perturbed by Ar are carried out using both close-coupling (CC) and coupled-states (CS) calculations. CS calculations are found to underestimate the cross sections by up to 15%. The effect occurs even for isotropic Raman cross sections, which are not affected by reorientation contributions. The discrepancy arises mostly for collisions with large orbital angular momenta l , occurring on the long-range part of the potential. It may be attributed to collisions that are adiabatic rather than sudden in nature. A hybrid computational method, employing CS calculations for low l and decoupled l -dominant (DLD) calculations for high l , offers a promising solution. © 1999 American Institute of Physics. [S0021-9606(99)00735-7]

I. INTRODUCTION

The effects of pressure on the shapes of infrared absorption lines are important in atmospheric modeling, especially in the analysis of data from satellite-based remote sensing instruments. Experimentally, it is difficult to measure line shape parameters (widths, shifts, and mixing coefficients) to the accuracy needed, especially at low temperatures. It is therefore desirable to develop reliable methods for calculating the parameters from potential energy surfaces. However, even for pressure-broadening coefficients, the classical path methods commonly used¹⁻³ involve a large number of approximations that have never been tested on realistically sized systems. For other parameters, such as those characterizing line shifts and line mixing, the situation is even less satisfactory. As a first step to allow us to assess the various theoretical methods in use, we have recently carried out benchmark calculations⁴ of pressure broadening of CO₂ infrared lines by Ar, using fully quantal scattering calculations on potential energy surfaces fitted to the spectra of van der Waals complexes.

Fully quantal calculations may be carried out in a variety of ways. Our initial expectation was that calculations employing either the inexpensive infinite-order-sudden (IOS) approximation⁵ or the more accurate coupled-states or centrifugal sudden (CS) approximation⁶ would be adequate for pressure-broadening cross sections in systems containing CO₂, which has a rotational constant of only 0.39 cm⁻¹. However, we quickly found that IOS calculations gave line-widths that drop off only very slowly with j , in contrast to both experiment and more sophisticated calculations.⁷ We therefore carried out extensive CS calculations of the pressure broadening, which have been reported separately.⁴

It would be in principle be preferable to carry out benchmark quantal calculations using close-coupling (CC) calculations,⁸ which make no dynamical approximations at all. Unfortunately, for a system as heavy as CO₂-Ar, it is currently prohibitively expensive to carry out such calculations at the very large number of energies needed for full line shape calculations. Nevertheless, it is feasible to carry out CC calculations for a limited number of energies, and we have undertaken this as a “spot check” on the more extensive CS results. In doing this, we discovered some unexpected features of the CC/CS comparison, and the purpose of this paper is to report them.

II. INFRARED LINEWIDTH CALCULATIONS

The pressure-induced width and shift of an isolated spectroscopic line are related to the real and imaginary parts of the (thermally averaged) line shape cross section. In the impact approximation, the line shape cross section may be calculated in terms of S -matrix elements for the molecular collisions involved. The CC⁸ and CS⁶ expressions for the line shape cross sections are

$$\begin{aligned} \sigma_{CC}^{(q)}(\mathbf{v}_a j_a; \mathbf{v}_b j_b; E_{\text{kin}}) \\ = (\pi/k^2) \sum_{J_a J_b l l'} (2J_a + 1)(2J_b + 1) \left\{ \begin{matrix} j_a & q & j_b \\ J_b & l & J_a \end{matrix} \right\} \\ \times \left\{ \begin{matrix} j_a & q & j_b \\ J_b & l' & J_a \end{matrix} \right\} [\delta_{ll'} - \langle \mathbf{v}_a j_a l' | S^{J_a}(E_{\text{kin}} + E_a) | \mathbf{v}_a j_a l \rangle \\ \times \langle \mathbf{v}_b j_b l' | S^{J_b}(E_{\text{kin}} + E_b) | \mathbf{v}_b j_b l \rangle^*], \end{aligned} \quad (1)$$

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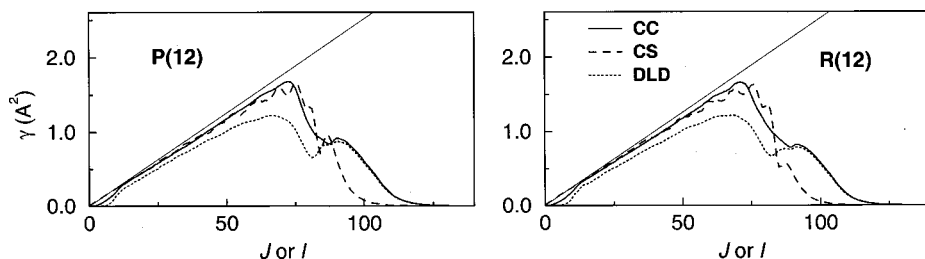


FIG. 1. Partial linewidth cross sections for the infrared $P(12)$ and $R(12)$ lines of CO_2 perturbed by Ar from CC, CS, and DLD calculations at $E_{\text{kin}}/hc = 200 \text{ cm}^{-1}$.

$$\begin{aligned} \sigma_{\text{CS}}^{(q)}(v_a j_a; v_b j_b; E_{\text{kin}}) \\ = (\pi/k^2) \sum_{l \lambda_a \lambda_b} (2l+1) \left[1 - \begin{pmatrix} j_a & q & j_b \\ -\lambda_a & \lambda_a - \lambda_b & \lambda_b \end{pmatrix}^2 \right. \\ \times \langle v_a j_a | S^{l \lambda_a}(E_{\text{kin}} + E_a) | v_a j_a \rangle \\ \left. \times \langle v_b j_b | S^{l \lambda_b}(E_{\text{kin}} + E_b) | v_b j_b \rangle^* \right], \end{aligned} \quad (2)$$

where q is the tensor order of the spectroscopic transition (0 for isotropic Raman, 1 for infrared, 2 for anisotropic Raman). The two states involved in the spectroscopic transition are described by vibrational and rotational quantum numbers v_a, j_a and v_b, j_b , and $E_{\text{kin}} = \hbar^2 k^2 / 2\mu$ is the kinetic energy of the collision; note that the two S matrices are in general evaluated at *different* total energies. The individual CC S -matrix elements are also labeled by the total angular momenta, J_a and J_b , and the orbital angular momenta before and after the collision, l and l' . In the CS case, $l = l'$ and there is an additional label λ , which is the projection of j onto the intermolecular axis. Equation (2) is actually the “ l -labeled” CS expression,⁶ which has been shown to be much more accurate than the “ J -labeled” expression.⁹

We began by carrying out CC and CS calculations for the infrared $P(12)$ and $R(12)$ lines of CO_2 in Ar at a kinetic energy corresponding to 200 cm^{-1} , which is near the peak in the room-temperature relative velocity distribution. The potential energy surface used was the “single repulsion” potential of Hutson *et al.*,¹⁰ which was recently determined by fitting potential parameters to the spectra of the Ar- CO_2 van der Waals complex and second virial coefficients of Ar + CO_2 mixtures; the functional form is based on the “systematic model” of Wheatley and Price¹¹ but incorporates a two-site model of the dispersion energy. In the present work, the CO_2 rotational constant was taken to be 0.3902 cm^{-1} , so scattering calculations were required at total energies $E_{\text{tot}}/hc = 251.5, 260.9$, and 271.0 cm^{-1} , corresponding to the CO_2 $j = 11, 12$, and 13 levels, respectively. The basis set included all CO_2 rotor levels up to $j = 32$.

We were somewhat surprised to find that the CC linewidth cross sections are about 10% larger than the corresponding CS cross sections. For the $P(12)$ line, the values are 93.8 Å^2 (CC) and 84.6 Å^2 (CS). This discrepancy is larger than we expected on the basis of previous CC/CS comparisons.⁹ We therefore investigated the partial cross sections γ , which are the contributions from different partial waves: $\gamma_{\text{CC}}(J)$ is a function of the total angular momentum J for CC calculations, and $\gamma_{\text{CS}}(l)$ is a function of the orbital angular momentum l for CS calculations. In the CC case, we

define $\gamma_{\text{CC}}(J)$ as containing all the new contributions that arise when terms involving $S^J(E_{\text{kin}} + E_{j_a})$ and $S^J(E_{\text{kin}} + E_{j_b})$ are included in the sum. These are the terms with $J_a = J = J_b$, $J_a < J = J_b$ and $J_b < J = J_a$ in Eq. (1). The results obtained are shown in Fig. 1. It is useful to think of the partial cross sections in terms of an opacity $P(l)$, defined by

$$\gamma(l) = (2l+1)(\pi/k^2)P(l). \quad (3)$$

If the inelasticity is very strong, $P(l) = 1$: this corresponds to the “statistical” limit, and produces the partial cross sections shown as straight lines in Fig. 1.

It may be seen that the CC and CS partial cross sections are very similar to one another at J (or l) values up to about 80, and make contributions that are about 5 or 10% below the statistical limit. The discrepancy between the CC and CS results occurs mostly for the higher partial waves, J or $l > 100$: the CC contributions persist to considerably higher values of J or l . It must of course be remembered that, for CC calculations, there are channels for each J with values of l lying between $|J-j|$ and $(J+j)$, so that for $j=12$ a substantial range of l values is included for each J . Some “rounding off” of the CS high- l cutoff is thus to be expected in the CC results. Nevertheless, it is surprising that the *integrated* contribution from this region is so different in the two cases.

The CS approximation can be derived in several ways. One of these involves neglecting $\Delta\lambda$ transitions in a body-fixed frame aligned along the atom-molecule vector. This approximation is expected to be most accurate for small values of l , corresponding to collisions occurring on the short-range part of the potential. An alternative approximation, which has been less widely used but has had some success for systems dominated by long-range collisions, is the decoupled l -dominant (DLD) approximation,¹² which achieves a comparable simplification in a space-fixed frame. In the DLD approximation, coupling between channels $j\mathcal{L}$ and $j'\mathcal{L}$ is retained (where $\mathcal{L} = l + j - J$) but coupling between channels $j\mathcal{L}$ and $j'\mathcal{L}'$ (with $\mathcal{L}' \neq \mathcal{L}$) is neglected. This can be justified, for sufficiently large J values, by comparing the Percival-Seaton coefficients that scale the radial potential coefficients.

We have carried out DLD calculations on the $P(12)$ and $R(12)$ lines in CO_2 -Ar, and the results are included in Fig. 1. The DLD partial cross sections are substantially in error for low values of J , and the DLD integral cross section is considerably too low, as expected on the basis of earlier comparisons.⁹ Nevertheless, the DLD *partial* cross sections agree very well with the CC values for $J > 95$.

TABLE I. Linewidth cross sections for isotropic Raman lines of CO₂-Ar at $E_{\text{kin}}/hc=200$ cm⁻¹ (in Å²) using different computational methods. The quantities in brackets after the CS results show the change in cross section when the basis set is increased to include CO₂ rotor functions up to $j=40$.

Line	CC	CS	DLD
Q(0)	123.6	124.3 (+0.0)	93.0
Q(4)	103.7	99.7 (+0.0)	82.0
Q(8)	96.2	91.7 (+0.1)	76.8
Q(12)	89.3	77.9 (-0.2)	73.9
Q(16)	83.0	78.1 (+0.0)	69.4
Q(20)	77.8	77.2 (+0.4)	65.6

The presence of the angular momentum q complicates the interpretation of infrared ($q=1$) and anisotropic Raman ($q=2$) line shapes. However, for isotropic Raman lines, the equations simplify because $q=0$ and $j_a=j_b$. Under these circumstances, the linewidth cross sections may be rewritten in terms of state-to-state inelastic cross sections,

$$\sigma^{(0)}(j;j) = \sum_{j' \neq j} \sigma(j \rightarrow j'). \quad (4)$$

For infrared and anisotropic Raman lines, $q \neq 0$ and such a rearrangement is no longer possible. Nevertheless, the *approximation* is sometimes employed that¹³

$$\sigma^{(q)}(j_a;j_b) \approx \frac{1}{2} \left[\sum_{j' \neq j_a} \sigma(j_a \rightarrow j') + \sum_{j' \neq j_b} \sigma(j_b \rightarrow j') \right]. \quad (5)$$

The terms that are omitted in Eq. (5) are often described as “reorientation” contributions, though there is no short-cut to calculating them other than to evaluate both the exact and

approximate expressions for the cross sections. Green¹⁴ has shown that Eq. (5) can be a poor approximation for some systems.

It is important to understand whether the discrepancy observed here between CS and CC calculations arises from reorientation cross sections. We have therefore carried out similar linewidth calculations for isotropic Raman lines $Q(j)$. Such calculations are in fact relatively inexpensive, because the two S -matrices needed for each line are at the same total energy. We have carried out such calculations for $E_{\text{kin}}/hc=200$ cm⁻¹ for several values of j : the resulting CC, CS, and DLD cross sections are listed in Table I. It may be seen that the CS approximation is quite accurate (within 2%) for low j , but that there are errors of up to 13% at higher j values. Since the discrepancy between the CC and CS calculations exists even for isotropic Raman cross sections ($q=0$), it is clearly *not* associated with the reorientation contributions.

The partial wave contributions for some of the isotropic Raman cross sections are shown in Fig. 2. The general behavior is similar to that observed for infrared lines. For low values of J or l , the CS and CC partial linewidth cross sections again agree well, and for low j the contributions are close to the statistical limit of Eq. (3). For higher j , the partial cross sections still increase nearly linearly with J or l to begin with, but lie slightly below the statistical limit. The CC contributions lie further below the statistical limit for $J < j$, where there are fewer than $2j+1$ allowed values of l . Nevertheless, as for the $P(12)$ line, the major difference between CC and CS calculations occurs at high J or l , where the CS partial cross sections display a much sharper high- l cutoff.

The DLD integral cross sections are again quite poor,

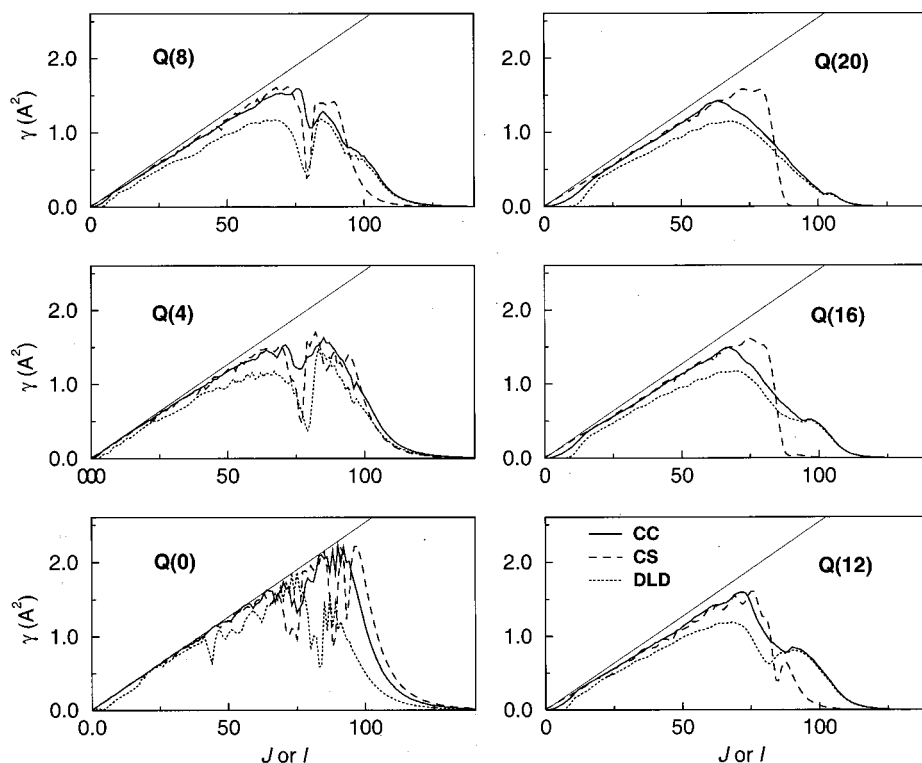


FIG. 2. Partial linewidth cross sections for the isotropic Raman lines $Q(j)$ of CO₂ perturbed by Ar from CC, CS, and DLD calculations at $E_{\text{kin}}/hc=200$ cm⁻¹.

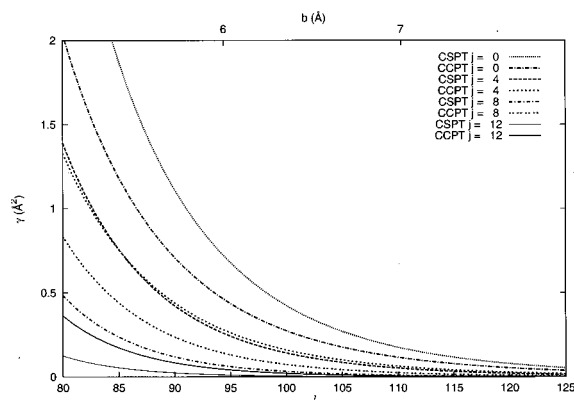


FIG. 3. Perturbative transition probabilities for inelastic cross sections in the straight-line classical path approximation at $E_{\text{kin}}/hc = 200 \text{ cm}^{-1}$.

and it may be seen in Fig. 2 that the DLD partial cross sections are substantially below the CC and CS results over most of the range of l . However, the DLD approximation actually performs quite well at high l , in just the region where the CS approximation breaks down.

Since the isotropic Raman cross sections can be written in terms of inelastic cross sections, we can use perturbation theory for the inelastic cross sections in the CC and CS approximations to explore the origin of the discrepancy. For an orbital angular momentum value $l \approx 80$, the classical impact parameter b is approximately 5 \AA at a translational energy corresponding to 200 cm^{-1} . Such collisions will sample primarily the weak long-range portion of the potential and will involve only small classical deflections. We therefore examine the transition probability, $P(j \rightarrow j'; b, v)$ between levels j and j' , at impact parameter b and speed v , using a straight-line classical path and first-order time-dependent perturbation theory.

Within the straight-line classical path approximation, Rabitz and Gordon¹⁵ have given analytical expressions for the state-to-state opacities (transition probabilities) in close-coupling calculations, and Dickinson and Richards¹⁶ have given analogous expressions for CS calculations. These results can be expressed as^{16,17}

$$P^{\text{CCPT}}(j \rightarrow j'; b, v) = \frac{1}{5}(2j' + 1) \begin{pmatrix} j & 2 & j' \\ 0 & 0 & 0 \end{pmatrix}^2 \times \left\{ \frac{1}{4}(V_{20}^2)^2 + \frac{3}{8}[(V_{22}^2)^2 + (V_{2-2}^2)^2] \right\}, \quad (6)$$

$$P^{\text{CSPT}}(j \rightarrow j'; b, v) = \frac{1}{5}(2j' + 1) \begin{pmatrix} j & 2 & j' \\ 0 & 0 & 0 \end{pmatrix}^2 (V_{20}^2)^2, \quad (7)$$

where

$$V_{\nu\mu}^\lambda = \frac{2}{\hbar} \int_0^\infty V_\lambda(R) \cos(\nu\omega t - \mu\phi(t)) dt. \quad (8)$$

Here, $V_\lambda(R)$ is the coefficient of $P_\lambda(\cos \theta)$ in the Legendre expansion of the potential and $\phi(t)$ is the plane polar angle of the atom, measured from the point of closest approach.¹⁶

To proceed analytically, we need a model of the potential surface. For this purpose, we employ

$$V(R, \theta) = -[C_6^{(0)} + C_6^{(2)}P_2(\cos \theta)]R^{-6}, \quad (9)$$

which is a reasonable approximation for long-range collisions. This potential allows the trajectory integrals $V_{\nu\mu}^\lambda$ to be evaluated in closed form.¹⁶ A fit to the true Ar-CO₂ potential for values of R between 6 and 7 \AA is given by $C_6^{(0)} = 151 E_h a_0^6$ and $C_6^{(2)} = 93 E_h a_0^6$.

The Q-branch partial cross sections from CCPT and CSPT calculations at $E_{\text{kin}}/hc = 200 \text{ cm}^{-1}$ on this potential are compared as a function of l for $l > 80$ in Fig. 3. The upper axis of Fig. 3 is labeled with the corresponding values of the impact parameter b . Within the classical path approximation, the results of both the CS and CC approximations depend naturally on l : the classical path CC results involve a sum over m_j at fixed l , rather than the sum over l from $|J-j|$ to $J+j$ involved in the quantal CC results [see Eq. (1)]. It should be recalled that, to facilitate an analytic treatment, these results use a simple approximation to the potential which is best for $6 \leq R \leq 7 \text{ \AA}$ and becomes increasingly inaccurate for smaller R and hence for collisions at smaller impact parameters. Furthermore, for trajectories that approach closer than $R \approx 5.5 \text{ \AA}$, the potential is sufficiently strong to perturb significantly the straight-line path assumed. The magnitudes of the classical path partial cross sections are smaller than those obtained from the quantal calculations (shown in Fig. 2). We attribute this to deficiencies in the potential approximation employed. However, the differences between the CC and CS results in the classical path and the quantal calculations behave similarly as j is increased. For $j=0$ the CS results exceed the CC results, for $j=4$ the two are very similar, while for $j \geq 8$ the CC results exceed the CS values. Hence the explanation for this behavior in the classical path results should help understand the corresponding differences in the quantal results.

A crucial role in the classical path approximation is played by the adiabaticity parameter, $z = \omega b/v$, where $\hbar\omega$ is the energy difference between levels j and j' . Small z values correspond to sudden collisions, where the rotor is almost stationary during the collision, while large z values correspond to adiabatic collisions, for which the transition probabilities fall off essentially exponentially with z . For example, the $j=12 \rightarrow 14$ transition with $E_{\text{kin}}/hc = 200 \text{ cm}^{-1}$ and $b = 6.5 \text{ \AA}$ has $z = 5.59$; thus the collisions of interest are almost adiabatic and hence are very sensitive to the rotation of the molecule during the collision.

The origin of the difference between the CC and CS results appears to be the substantial variation between the different $V_{2\mu}^2$ integrals, depending on whether the $\mu\phi(t)$ term in Eq. (8) adds to the $\nu\omega t$ term or cancels it. Since the cosine term gives rise to considerable cancellation, the CC opacity is dominated by the integral V_{22}^2 , for which $\nu\omega t$ and $\mu\phi(t)$ have opposite signs. In the CS approximation, this is replaced by a significantly smaller term, V_{20}^2 , which is independent of $\phi(t)$.

Since the effect arises primarily for adiabatic collisions, it will increase with increasing rotor level j . However, since the magnitude of the large $J(l)$ contribution decreases with increasing j (see Fig. 3), the error in the broadening cross section will ultimately decrease.

This physical effect will also apply to the dipole and the anisotropic Raman broadening, although the details will be quantitatively different. We have evaluated the dipole broadening for the infrared $P(12)$ line using the corresponding straight-line path and perturbation theory approximation.¹⁸ This gave comparable differences with the nonperturbative CC results.

Effects of this type have not been noticed before because previous calculations have concentrated on systems for which adiabatic collisions were less important. In particular, most previous CC calculations have been performed either for systems containing He atoms or for molecules with large rotor constants such as HF or HCl: in either case, the long-range forces were too weak to cause substantial inelasticity. Nevertheless, the effects found in the present work may be expected to be generally important in systems involving the interaction of molecules with large moments of inertia with heavy collision partners.

III. CONCLUSIONS

We have carried out benchmark close-coupling and coupled-states calculations of the pressure broadening of CO₂ infrared and Raman lines by Ar. We have found that the CS approximation is less accurate than expected, underestimating the broadening cross sections by up to 15%. This occurs because there are important contributions to the line broadening from inelastic collisions with large orbital angular momentum l (or classical impact parameter b) which occur on the long-range part of the potential, and the CS approximation breaks down for such collisions. Such effects may be expected to be important whenever the molecule concerned has a small rotational constant, so that even the long-range potential has sufficient anisotropy to cause inelastic collisions. This will include many molecules of atmospheric importance.

The effects identified here are not confined to pressure-broadening cross sections. They will also occur in inelastic cross sections and in the phenomenological cross sections that control transport and relaxation properties of gases. Since the effect is strongly l -dependent, it is likely to have a particularly important influence on differential cross sections.

We have investigated the origin of the effect using a method based on time-dependent perturbation theory and a straight-line classical path. The discrepancy arises mainly for collisions that are adiabatic rather than sudden.

The present work has concentrated on a limited number of lines and kinetic energies in order to make the calculations tractable. The calculations needed to simulate a complete spectrum, including thermal averaging, are much more extensive, and close-coupling calculations for this purpose are likely to remain prohibitively expensive in computational terms for some time to come. We have found that the decoupled l -dominant approximation, which is designed for collisions that take place on the long-range part of the potential, is quite accurate for line-broadening contributions at large l . An approach that appears to be promising is to use coupled-states calculations for small values of the orbital angular momentum l , and then switch over to decoupled l -dominant calculations for large l . However, the handling of the intermediate region and the identification of an appropriate l value at which to switch over require further work.

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